

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C07C 17/23, 19/08, 19/10	A1	(11) International Publication Number: WO 96/17813 (43) International Publication Date: 13 June 1996 (13.06.96)
(21) International Application Number: PCT/US95/15158 (22) International Filing Date: 21 November 1995 (21.11.95) (30) Priority Data: 08/351,908 8 December 1994 (08.12.94) US (71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventor: RAO, Velliyur, Nott, Mallikarjuna; 1 Georgetown Avenue, Wilmington, DE 19809 (US). (74) Agents: HEISER, David, E. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: HALOFLUOROCARBON HYDROGENOLYSIS (57) Abstract A highly selective process is disclosed for the hydrogenolysis of 2,2-dichlorohexafluoropropane (i.e., CFC-216aa or $\text{CF}_3\text{CCl}_2\text{CF}_3$) to 2,2-dihydrohexafluoropropane (i.e., HFC-236fa or $\text{CF}_3\text{CH}_2\text{CF}_3$) and 2-chloro-2-hydrohexafluoropropane (i.e., 226da or $\text{CF}_3\text{CHClCF}_3$). The process involves reacting the starting material with hydrogen at an elevated temperature of about 300 °C or less in the presence of a catalyst containing a catalytically effective amount of palladium supported on a support of fluorinated alumina and/or aluminum fluoride.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LJ	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

TITLE

HALOFLUOROCARBON HYDROGENOLYSIS

FIELD OF THE INVENTION

5 This invention relates to catalytic hydrogenolysis of halofluorocarbons; and more particularly to the hydrogenolysis of said materials using palladium-containing catalysts.

BACKGROUND

10 Various processes for the catalytic hydrogenolysis of chlorofluorocarbons and hydrochlorofluorocarbons are known. For example, British Patent Specification 1,578,933 illustrates that mixtures of $C_2Cl_2F_4$ isomers can be subjected to hydrogenolysis over a particulate catalyst of palladium on charcoal (which was intimately
15 mixed with glass helices to prevent clogging) or palladium on alumina, to mixtures of $C_2H_2F_4$ isomers. U.S. 2,942,036 discloses the reaction of 1,2,2-trichloropentafluoropropane with hydrogen in the presence of palladium on activated carbon catalyst to produce
20 1,2,2-trihydropentafluoropropane. The examples show that under the conditions of the experiments one of the products from this reaction is $CF_3CH=CF_2$. The carbon support may be treated with aqueous HF prior to depositing palladium on the support for the purpose of
25 removing silica from the carbon. U.S. 5,171,901 discloses inter alia the catalytic hydrogenation of $CF_3CCl_2CF_3$ and/or $CF_3CHClCF_3$ using suitable catalysts (e.g., palladium). Disclosed support materials include activated carbons, aluminas, silicas, barium sulfate,
30 spinels, silicates and titanium dioxide. Preferred supports are activated carbons and lithium/aluminum spinels. Examples are provided wherein 2,2,-dichlorohexafluoropropane and 2-chloro-2-hydrohexafluoropropane are hydrogenated using palladium supported
35 on globular lithium/aluminum spinel. Japanese Patent Application Publication Hei 1(1989)-319441 discloses a process where one chlorine atom is selectively replaced by hydrogen in 1,1,1-trichlorotrifluoroethane using a

platinum catalyst. For comparison, a palladium on carbon catalyst is disclosed to produce 1,1,1-trifluoroethane as the major product under the conditions of the experiment.

5

SUMMARY OF THE INVENTION

The present invention provides a process for the hydrogenolysis of 2,2-dichlorohexafluoropropane (i.e., CFC-216aa or $\text{CF}_3\text{CCl}_2\text{CF}_3$) to 2,2-dihydrohexafluoropropane (i.e., HFC-236fa or $\text{CF}_3\text{CH}_2\text{CF}_3$) and 2-chloro-2-hydrohexafluoropropane (i.e., 226da or $\text{CF}_3\text{CHClCF}_3$). The process comprises reacting said starting material with hydrogen at an elevated temperature of about 300°C or less in the presence of a catalyst containing a catalytically effective amount of palladium supported on a support selected from the group consisting of fluorinated alumina, aluminum fluoride and mixtures thereof.

10

15

DETAILED DESCRIPTION

The catalysts suitable for the process of this invention comprise palladium. The palladium is supported on fluorinated alumina, aluminum fluoride and/or a mixture thereof. Preferred catalysts consist essentially of palladium on an aluminum fluoride or fluorinated alumina support. The procedure for preparing such a catalyst is described in U.S. 4,873,381, the entire contents of which are hereby incorporated herein by reference.

20

25

The concentration of palladium on the fluorinated alumina and/or aluminum fluoride support is typically within the range of from 0.1 to 10% by weight of the catalyst. The support can be prepared by fluorination of alumina at elevated temperatures. It is preferred that the fluorine content of the support be sufficient to provide a fluorine to aluminum atomic ratio of at least 2.4. The aluminum fluoride or fluorinated alumina support utilized in the instant invention has the advantage of being regeneratable by conventional means, which carbon-based supports do not have. For example, $\text{CF}_3\text{CCl}_2\text{CF}_3$ can be reacted with hydrogen over a catalyst

30

35

of this invention until the conversion rate of CFC-216aa decreased by at least about 20 percent compared to the conversion rate of CFC-216aa using fresh catalyst at the same conditions; and the catalyst can then be
5 regenerated (e.g., by first treating with air or oxygen at elevated temperature, and then reducing with hydrogen).

The reaction temperature is typically within the range of from about 100°C to about 300°C. A preferred
10 range is from about 100°C to 250°C. Generally, in order to provide substantial hydrogenolysis product yields, the amount of hydrogen used is at least about 0.5 mole per mole of the CFC-216aa starting material. To provide yields desired in many embodiments, at least
15 stoichiometric amounts of hydrogen are used. A considerable excess of hydrogen can also be advantageously employed to provide the yields desired in many embodiments in addition to serving as a heat sink to reduce the overall temperature rise in the reactor.
20 The three-carbon hydrogenolysis product from the hydrogenolysis of CFC-216aa contains at least 90% of the fluorine atoms contained in the CFC-216aa reacted and less than 5 mole percent of said product contains 5 fluorine substituents.

25 CFC-216aa utilized in this process can be made by conventional means which are well known to the art (see, e.g., U.S. Patent No. 5,068,472).

The hydrogenolysis of 2,2-dichlorohexafluoropropane with hydrogen may be conducted in any suitable reactor,
30 including fixed and fluidized bed reactors. The reaction vessel should be constructed from materials which are resistant to the corrosive effects of hydrogen halide.

Pressure is not critical. Atmospheric and
35 superatmospheric pressures are the most convenient and are therefore preferred.

Unreacted 2-chloro-2-hydrohexafluoropropane may be recycled to the reactor to produce additional quantities

of 2,2-dihydrohexafluoropropane or be used as an organic intermediate to produce 2-hydroheptafluoropropane.

HFC-236fa is useful as a refrigerant, fire extinguishant, heat transfer medium, gaseous dielectric, sterilant carrier, polymerization medium, particulate removal fluid, carrier fluid, buffing abrasive agent, displacement drying agent and power cycle working fluid. In particular, HFC-236fa is a highly effective refrigerant.

The present process has the advantage that the desirable products are obtained in extremely high selectivity.

Practice of the invention will become further apparent from the following non-limiting examples.

EXAMPLES

Preparation of Palladium on Fluorinated Alumina

Commercial 0.5 weight percent palladium on alumina (21.4 g, 1.6 mm extrudates) was placed in a reactor and heated to 175°C in a flow of nitrogen (20 cc/min.) for about 2 hours. At the end of this period the nitrogen flow was increased to 50 cc/min. and an HF flow (50 cc/min.) was passed through the reactor. After the initial exotherm subsided (about three hours), the nitrogen flow was reduced to 20 cc/min. and the HF flow increased to 80 cc/min. The reactor temperature was then gradually increased to about 400°C over about a five hour period and maintained at 400°C for an additional 30 minutes. The HF flow was then stopped and the reactor purged with nitrogen. The palladium on fluorinated alumina prepared by this method was used in the hydrogenolysis experiment below.

Hydrogenolysis of CFC-216aa using Palladium on Fluorinated Alumina Catalyst

Run No. 1 - Liquid CFC-216aa (3 mL/hour) was vaporized and mixed with 20 cc/minute of hydrogen. This vapor mixture was sent through a 0.5" (12.7 mm) O.D. x 8" (203 mm) Hastelloy™ nickel alloy reactor containing 15.5 g of the palladium on fluorinated alumina catalyst

maintained at 150°C using a fluidized sand bath. After nine hours of operation under these conditions, organic product analysis using conventional gas chromatography indicated that CFC-216aa conversion was essentially
5 complete. The hydrogen-containing products included 32.4% HFC-236fa (2,2-dihydrohexafluoropropane) and 64.5% HCFC-226da (2-chloro-2-hydrohexafluoropropane) in addition to very small quantities of other products.

Run No. 2 - Run No. 1 was repeated except that the
10 temperature was 200°C. After about 15 hours of operation, CFC-216aa conversion was still complete. The organic hydrogen-containing products included 45.5% HFC-236fa and 52% HCFC-226da.

Run No. 3 - Run No. 2 was repeated except that the
15 hydrogen flowrate was increased to 40 cc/minute. The CFC-216aa conversion was complete. The organic hydrogen-containing products included 48.9% HFC-236fa and 49.4% HCFC-226da.

Run No. 4 - Run No. 3 was repeated except that the
20 temperature was increased to 250°C. The organic hydrogen-containing products included 64.5% HFC-236fa and 28.0% HCFC-226da.

Run No. 5 - Run No. 4 was repeated except that the hydrogen flow rate was reduced to 20 cc/min. CFC-216aa
25 conversion was complete. The organic hydrogen-containing products included 63.1% HFC-236fa and 30.1% HCFC-226da.

Comparative Hydrogenolysis of CFC-216aa using Palladium
on low-ash acid-washed carbon

30 Carbon Support

The carbon support used in the examples was a 4 x 8 mesh (about 4.7 mm x. 2.4 mm) commercial grade coconut shell carbon which had (before washing) an ash content of about 2.6 weight percent. After hydrochloric acid
35 washing, the carbon support had an ash content of less than about 0.1 weight percent.

Run No. 6 - Liquid CFC-216aa (3 mL/hour) was vaporized and mixed with 10 cc/minute of hydrogen. This

vapor mixture was sent through a 0.5" (12.7 mm) O.D. x 8" (203 mm) Hastelloy™ nickel alloy reactor containing 7.2 g of 0.5 weight percent palladium supported on low-ash, acid-washed carbon maintained at 150°C using a fluidized sand bath. Organic product analysis using conventional gas chromatography indicated that about 90% of the starting material had been converted. The hydrogen-containing products included 15.7% 2,2-dihydrohexafluoropropane (HFC-236fa), 54.3% 2-chloro-2-hydrohexafluoropropane (HCFC-226da), 12.3% 2-hydropentafluoropropene, and 1.7% 1,2,2-trihydropentafluoropropane (HFC-235fa) and small quantities of other compounds.

Run No. 7 - Run No. 6 was repeated except that the hydrogen flowrate was increased to 30 cc/minute. Organic product analysis using conventional gas chromatography indicated that the starting material conversion was essentially complete. The hydrogen-containing products included 24.8% 2,2-dihydrohexafluoropropane (HFC-236fa), 54.6% 2-chloro-2-hydrohexafluoropropane (HCFC-226da) and 19.8% 1,2,2-trihydropentafluoropropane (HFC-235fa) and small quantities of other compounds.

This comparative experiment illustrates that when using palladium supported on acid-washed carbon as catalyst for the hydrogenolysis of CFC-216aa (where two chlorines of the starting compound are on the middle carbon and the two adjacent carbons contain trifluoromethyl groups) an olefin and/or a saturated product containing one less fluorine than the starting compound can be produced in significant amounts.

WHAT IS CLAIMED IS:

1. A process for the hydrogenolysis of 2,2-dichlorohexafluoropropane to 2,2-dihydrohexafluoropropane and 2-chloro-2-hydrohexafluoropropane which
5 comprises
 reacting said starting material with hydrogen at an elevated temperature of about 300°C or less in the presence of a catalyst containing a catalytically effective amount of palladium supported on a support
10 selected from the group consisting of fluorinated alumina, aluminum fluoride and mixtures thereof.
2. The process of Claim 1 wherein the catalyst consists essentially of palladium on an aluminum fluoride support.
- 15 3. The process of Claim 2 wherein the concentration of palladium on the support is within the range of from 0.1 to 10% by weight of the catalyst.
4. The process of Claim 1 wherein the catalyst consists essentially of palladium on a fluorinated
20 alumina support.
5. The process of Claim 4 wherein the concentration of palladium on the support is within the range of from 0.1 to 10% by weight of the catalyst.
6. The process of Claim 5 wherein the fluorine to
25 aluminum atomic ratio of said support is at least 2.4.
7. The process of Claim 1 wherein the temperature is from about 100°C to 250°C.
8. The process of Claim 1 wherein the three-carbon hydrogenolysis product from the hydrogenolysis of
30 $\text{CF}_3\text{CCl}_2\text{CF}_3$ contains at least 90% of the fluorine atoms contained in the $\text{CF}_3\text{CCl}_2\text{CF}_3$ reacted and less than 5 mole percent of said product contains 5 fluorine substituents.
9. The process of Claim 1 wherein $\text{CF}_3\text{CCl}_2\text{CF}_3$ is
35 reacted with hydrogen until the conversion rate of $\text{CF}_3\text{CCl}_2\text{CF}_3$ decreases by at least about 20 percent compared to the conversion rate of $\text{CF}_3\text{CCl}_2\text{CF}_3$ using fresh

catalyst at the same operating conditions; and wherein the catalyst is regenerated.

10. the process of Claim 9 wherein the catalyst consists essentially of palladium on an aluminum
5 fluoride or fluorinated alumina support; and wherein the concentration of palladium on said support is within the range of from 0.1 to 10% by weight of the catalyst.

INTERNATIONAL SEARCH REPORT

 Internat Application No
 PCT/US 95/15158

 A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C07C17/23 C07C19/08

C07C19/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 349 115 (E.I. DU PONT DE NEMOURS AND COMPANY) 3 January 1990 cited in the application see the whole document ---	1-7
Y	EP,A,0 442 075 (BAYER AG) 21 August 1991 cited in the application see the whole document ---	1-7
Y	WO,A,90 08748 (E.I. DU PONT DE NEMOURS AND COMPANY) 9 August 1990 see claims ---	1-7
Y	EP,A,0 539 989 (HOECHST AKTIENGESELLSCHAFT) 5 May 1993 see the whole document -----	1-7



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

29 March 1996

Date of mailing of the international search report

03.04.96

Name and mailing address of the ISA

 European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
 Fax (+ 31-70) 340-3016

Authorized officer

Bonnevalle, E

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat Application No

PCT/US 95/15158

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-349115	03-01-90	US-A- 4873381	10-10-89
		AU-B- 613296	25-07-91
		AU-B- 3488989	23-11-89
		DE-T- 68907808	27-01-94
		ES-T- 2058523	01-11-94
		JP-A- 2067235	07-03-90
		SU-A- 1757457	23-08-92

EP-A-442075	21-08-91	DE-A- 4004495	22-08-91
		CA-A- 2036220	15-08-91
		ES-T- 2044382	01-01-94
		JP-A- 4211027	03-08-92
		US-A- 5171901	15-12-92

WO-A-9008748	09-08-90	AT-T- 107270	15-07-94
		AU-B- 633295	28-01-93
		AU-B- 4840490	24-08-90
		CA-A- 2009188	03-08-90
		DE-D- 69009980	21-07-94
		DE-T- 69009980	12-01-95
		EP-A- 0449977	09-10-91
		JP-T- 4503209	11-06-92
		RU-C- 2026279	09-01-95
		US-A- 5068473	26-11-91
		US-A- 5146018	08-09-92

EP-A-539989	05-05-93	CA-A- 2081813	02-05-93
		JP-A- 5221894	31-08-93
